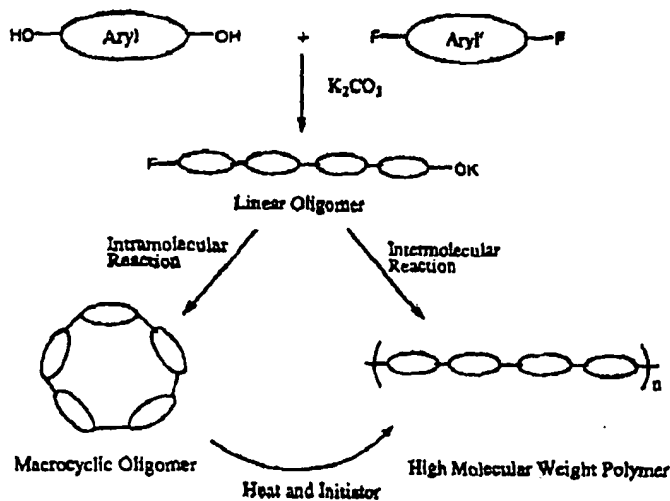




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(54) Title: CYCLIC OLIGOMER NANOCOMPOSITES



Schematic of the Formation of Macrocyclic and Linear Polymer

## (57) Abstract

The present invention features nanocomposites and methods for making same. The methods include combining at least one type of cyclic oligomer and at least one type of layered silicate under conditions which facilitate making the nanocomposite. The present invention has a variety of important uses including enhancing nanocomposite processing and providing nanocomposites with exceptional performance characteristics.

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## CYCLIC OLIGOMER NANOCOMPOSITES

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### CROSS-REFERENCE TO RELATED APPLICATION

The present application is a continuation-in-part of United States provisional application USSN 60/105433 entitled "Cyclic Oligomer Nanocomposites" and filed on October 23, 1998; the disclosure of which application is hereby incorporated by reference.

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### STATEMENT OF U.S. GOVERNMENT INTEREST

Funding for the present invention was provided in part by the Government of the United States by virtue of contract No. \_ from the U.S. Air Force. Thus, the Government of the United States has certain rights in and to the invention claimed herein.

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#### 1. FIELD OF THE INVENTION

The present invention features nanocomposites and methods for making same. The methods include combining a cyclic oligomer and a layered silicate under conditions which facilitate making the nanocomposite. The present invention has a variety of important uses including enhancing processing of the nanocomposite as well as providing nanocomposites with exceptional performance characteristics.

20

#### 2. BACKGROUND OF THE INVENTION

A nanocomposite has been defined as an interacting mixture of two phases, one of which is in the nanometer size range in at least one dimension. Due to the nanoscale dimensions of the reinforcement phase, nanocomposites have been reported to display highly desirable properties when compared to micro- or macro-composites. Accordingly, nanocomposites have been used to make a variety of new materials including those used in mechanical, optical, magnetic and dielectric applications. See generally Rouhi, A. M. in Nanotechnology, *Chem. & Engineering* (April 20, 1998) 57.

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Polymer/inorganic nanocomposites have attracted more particular attention. For example, the nanocomposites often provide for enhancement of

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polymer properties beyond what is achievable from more conventional particulate filled or micro-composites. These nanocomposites can include layers of mica-type silicates to provide inorganic reinforcement. Layered silicate-polymer nanocomposites having (i) polymer chains intercalated between the silicate layers or (ii) individual silicate layers delaminated and dispersed in a continuous polymer matrix are known in the field.

Methods for making the nanocomposites often include use of an organic surfactant such as alkyl ammonium. There have been reports that use of the surfactant significantly increases many performance advantages for a variety of commodity polymers.

However, there is recognition that prior methods for making nanocomposites have substantial shortcomings. For example, it is increasingly apparent that prior methods typically suffer from less than optimal dispersal between the polymer and layered silicate. Melt-processing and flow characteristics of the resulting mixture have also suffered. These difficulties have hindered good processing of the nanocomposites particularly at low temperatures of about 200 °C . Nanocomposites made under these conditions typically exhibit many undesirable properties.

There have been some attempts to address these shortcomings. For example, there have been efforts to make nanocomposites by using solvent and/or high pressure manipulations to optimize processing of the polymer and silicate material. However these methods are not always suitable.

For example, many solvents can be toxic and use of high pressure can significantly complicate manufacturing steps. Some or all of the nanocomposite components may be degraded by prolonged exposure to the solvents and high pressure and temperature. In addition, the attempts have been associated with formation of polymer voids.

Accordingly, it would be desirable to have effective methods of making nanocomposites that provide for good dispersal between the polymer and layered silicate material especially at low manufacturing temperatures of about 200°C. It would also be desirable to have essentially solvent-free methods that provide good melt-processing and flow characteristics for a wide variety of

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polymers and layered silicates. Further desirable would be to have nanocomposites made by the methods that provide exceptional performance characteristics.

## 5 SUMMARY OF THE INVENTION

The present invention features nanocomposites and methods for making same. In general, the methods include combining at least one type of cyclic oligomer with at least one type of layered silicate under conditions conducive to making the nanocomposite. In one embodiment of the method, the cyclic  
10 oligomer is a macrocycle and the method involves opening the macrocycle and polymerizing the opened macrocycle to produce a suitable nanocomposite polymer. In another embodiment of the method, the cyclic oligomer is a polycycle and the method involves combining the polycycle with at least one low melt viscosity polymer to form another suitable nanocomposite polymer.

15 Preferred use of the invention substantially reduces polymer void, enhances melt-processing, and improves flow characteristics. Significantly, many prior extrusion problems are avoided. The polymers can be used to produce nanocomposites having a variety of high performance features including good hardness, strong cross-linking and favorable ablative properties.

20 More particularly, we have found methods of making nanocomposites that provide good dispersal of components especially at "low" manufacturing temperatures of about 200°C or less. This feature of the invention provides several advantages. For example, it simplifies processing steps and can significantly preserve integrity of components used to make the nanocomposites.

25 Also, use of toxic solvent and/or high pressure manipulations is often avoided. Preferred practice of the methods generally enhances melt-processing and provides for more desirable viscosity conditions especially when extruder implementations are employed.

30 As illustrated below, the invention is generally compatible with use of a spectrum of polymer precursors, polymers and layered silicates. In particular, the methods of this invention are highly flexible and can be readily tailored to produce nanocomposites with performance characteristics well-suited for an

intended application.

A suitable polymer precursor for use with this invention is usually a monomer of a high molecular weight polymer ("polymer monomer"). A preferred polymer monomer is one capable of forming a linear oligomer which in most embodiments of this invention will include from between about 2 to about 25 monomers with about 3 to about 5 monomers being preferred for many applications.

Although a wide variety of linear oligomers are suitable for use with this invention, two types are specifically preferred.

The first type of linear oligomer is capable of undergoing intramolecular cyclization to form a macrocycle (sometimes referred to herein as a macrocyclic oligomer). In broad terms, the macrocycle includes repeating linear oligomers linked together to form a single ring member.

The second type of linear oligomer is capable of being cyclized under appropriate reaction conditions so that the oligomer includes at least one new ring member. That is, in the second oligomer type, one or more ring members are added to the oligomer under conditions in which the oligomer maintains an essentially linear form. In contrast, in the first type of linear oligomer, the macrocycle is formed by linking the oligomers together to form a single and large ring member, ie., an essentially circular macrocycle.

More particularly, and with respect to the second type of linear oligomer, that oligomer is sometimes referred to herein as a polycycle to specify that the added ring member may be the same as or different from one or more pre-existing ring members of the linear oligomer.

Illustrative polymer monomers for use with the invention are typically inexpensive and relatively easy to procure and/or to make, thereby providing a convenient processing route to a desired high performance polymer system. Several particular polymer systems for making the nanocomposites of this invention are provided below.

A generally preferred macrocycle for use with this invention is labile under pre-determined reaction conditions. Particularly, the macrocycle is often thermally labile although lability with respect to at least one of heat, light, sound,

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and chemical reaction of one or more labile side groups may be appropriate for some applications. More particularly, exposure to preferred reaction conditions "breaks" or "opens" the macrocycle which conditions also facilitate ring-opened polymerization of the opened ring member. Preferred ring-opened polymerization is linear although non-linear polymerization may be useful in some embodiments of this invention.

A more preferred macrocyclic oligomer undergoes temperature-assisted opening of the macrocycle and linear polymerization of the "opened" ring member. By the term "ring-opening" or related phrase is meant that at least one covalent bond of the ring member is broken under reaction conditions facilitating production of a desired linear polymerization intermediate. A preferred covalent bond is preferably thermally labile especially in the context of the macrocycle. More preferred covalent bonds include at least one of an ether, keto, or ester bond which bonds can typically link subunits of the ring member.

It will be apparent that it will sometimes be useful to make nanocomposites by using the linear oligomer as starting material. For example, the linear oligomer may be commercially available or it may be readily made from available reagents. In one embodiment, the linear oligomer is combined in the method with at least one type of layered silicate under conditions conducive to making the macrocyclic oligomer. In another embodiment, the same or different linear oligomer can be reacted under conditions which form a suitable polycyclic oligomer. Accordingly, significant use of polymer monomer can be reduced and sometimes eliminated by practice of this invention.

It will also be apparent that a linear oligomer generally described above can have at least one type of reiterative monomer unit and particularly one, two or three of such units. Thus in one embodiment, the macrocycle includes at least one type of repeating monomer subunit which subunit is preferably compatible with linear polymerization in accord with this invention. In another embodiment, the linear polycyclic oligomer can also have at least one type of reiterative monomer unit. As will be described below, the linear polycyclic oligomer is preferably melted and cross-linked with at least one suitable low melt viscosity polymer. Choice of a particular polymer monomer or oligomer will be guided by several

parameters including the type of nanocomposite desired.

More particularly, the present invention features methods for fabricating high use-temperature nanocomposites by using macrocyclic oligomers as illustrative starting materials. The methods are generally compatible with use of a variety of layered silicate materials including those natural and synthetic clays specified below.

Accordingly, and in one aspect, the invention features methods of making a nanocomposite. Such methods are sometimes referred to herein as "macrocyclic methods" or by a related term or phrase. In one embodiment, the method includes at least one of and preferably all of the following steps:

- a) cyclizing at least one type of linear oligomer under conditions that form at least one type of macrocyclic oligomer,
- b) combining the macrocyclic oligomer with at least one type of layered silicate to make an admixture,
- c) opening the macrocyclic oligomer to make a linear polymer intermediate,
- d) polymerizing the intermediate to make a polymer; and
- e) producing the nanocomposite from the admixture.

In a particular embodiment of the method, the method further includes making the linear oligomer by polymerizing at least one type of polymer monomer. That polymerization can be conducted along lines known in the field as linear polymerization or a related term or phrase.

The cyclization step of the method can be performed by one or a combination of different strategies that generally favor intramolecular instead of intermolecular reaction. In one embodiment, the method further includes diluting the linear oligomer (or mixture thereof) in a suitable solvent, wherein the ratio of the solvent to the linear oligomer is from between about 1.5 to about 25 (v/v). Preferably, the cyclization step further includes adding a suitable buffer, wherein the ratio of the buffer to the solvent is between from about 1.5 to about 5 (v/v). More specific information relating to the cyclization step and preferred buffers are provided below.

As also discussed, the present invention can be used with a wide variety of



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suitable polymer monomers and/or linear oligomers. In one embodiment, the linear oligomer includes at least one optionally substituted aryl group which linear oligomer can further include at least one optionally substituted heterocyclic group.

In another embodiment of the method, the macrocyclic oligomer has a  
5 molecular weight of from between about 2 to about 25 times the molecular weight of the linear oligomer employed in the method. Preferred is a macrocyclic oligomer having a ring member that includes from between about 2 to about 25 linear oligomers, preferably between from about 5 to about 10 linear oligomers. Additionally preferred macrocyclic oligomers include at least one of PEI,  
10 polyimide, polysulfone, or polycarbonate monomer. More specific macrocyclic oligomers for use in the method including methods for making and using same are disclosed below.

In another embodiment of the method, the layered silicate includes at least one of ORMLAS and a natural clay. A generally preferred nanocomposite  
15 produced includes one of the ORMLAS or natural clay, however combinations thereof may be suitable for some applications. The specific amount of the layered silicate to use in the method will be informed by, e.g., intended use and processing conditions desired. For many applications from between about 0.1% to about 10% (w/v) of the layered silicate in the nanocomposite will often be very useful.

20 A suitable nanocomposite produced in the method typically includes polymer that is intercalated or exfoliated within layers of the silicate. Preferred is a nanocomposite exhibiting a d-spacing of at least about 18 Angstroms as determined by X-ray diffraction (XRD). More specific nanocomposites are provided below.

25 In a more particular embodiment, the macrocyclic method is essentially performed in an extruder implementation and more specifically a standard extruder. In particular, the nanocomposite is produced by outputting the admixture from the extruder. Suitable extrusion methods for producing the nanocomposite are provided below.

30 For most applications, it will be useful to make the macrocyclic oligomer before adding the layered silicate and making the admixture. Although less preferred, it may be useful in some instances to make the admixture prior to

performing the cyclization step, e.g., by combining the linear oligomer with the layered silicate prior before cyclizing the oligomer in step a) of the method to make the macrocycle.

5       Methods for determining whether a particular linear oligomer has cyclized in the method are known in the field and include mass spectroscopy (MS) as discussed below. Methods for identifying formation of the linear polymer intermediate are also known and include detecting presence of polymerization and particularly identifying formation of high molecular weight polymer in the admixture.

10       In another aspect, the invention features methods for making a nanocomposite that include use of a suitable polycyclic oligomer. Such methods are sometimes referred to herein as "polycyclic oligomer" methods or a related term or phrase. In one embodiment, the method includes at least one of and preferably all of the following steps:

- 15       a) making at least one polycyclic oligomer preferably from at least one linear oligomer,
- b) combining the polycyclic oligomer with at least one low melt viscosity polymer and at least one inorganic layered silicate to make an admixture,
- c) melting the polycyclic oligomer and the low melt viscosity polymer in  
20       the admixture, preferably at a temperature of from between 175°C to about 275°C,
- d) cross-linking the polycyclic oligomer and the low melt viscosity polymer, preferably at a temperature of from between about 300°C to about 450°C; and
- 25       e) producing the nanocomposite from the admixture.

In one embodiment, the method further includes making the linear oligomer by polymerizing at least one type of polymer monomer.

In another embodiment, the polycyclic oligomer is made by combining the linear oligomer with at least one type of phosphite having the following general  
30       formula:  $X_1-(P=O)-X_2-R$ ; wherein each of  $X_1$  and  $X_2$  is selected individually from the following group: F, Cl, and Br, and R is an optionally substituted aryl or alkyl

group. Typically, one phosphite type will be employed in the method.

A preferred linear oligomer for use in the polycyclic method includes at least one optionally substituted aryl group which oligomer may further include at least one optionally substituted heterocyclic group.

5 More preferred linear oligomers for use in the polycyclic method are well-suited for intended use and have a molecular weight of from between about 500 to about 5000. A preferred polycyclic oligomer has a molecular weight approximating that of the linear oligomer, typically from between about 500 to about 5500.

10 In another embodiment of the polycyclic method, the layered silicate includes at least one of ORMLAS and a natural clay. For many applications, the nanocomposite produced in the method will include ORMLAS or natural clay however combinations thereof may be suitable for some applications of the invention. The amount of the layered silicate to use in the method will be  
15 informed by the intended use of the nanocomposite and the processing conditions desired. However for many applications from between about 0.1% to about 10% (w/v) of the layered silicate in the nanocomposite will be generally preferred.

A suitable nanocomposite produced in the polycyclic method includes polymer that is preferably intercalated or exfoliated within layers of the silicate.  
20 Preferred is a nanocomposite exhibiting a d-spacing of at least about 18 Angstroms as determined by X-ray diffraction (XRD). More specific nanocomposites made by the polycyclic route are provided below.

In a more particular embodiment, the polycyclic method is essentially performed in an extruder implementation and more specifically a standard  
25 extruder. In particular, the nanocomposite is produced by outputting the admixture from the extruder. Suitable extrusion methods for producing the nanocomposite are provided below.

In another aspect of this invention, there is provided a nanocomposite made by the methods of this invention. In particular, the invention provides highly  
30 useful nanocomposites made by the macrocyclic or polycyclic routes summarized above.

A wide spectrum of polymer monomers are suitable for use in the

macrocyclic and polycyclic methods generally described above. Thus in one embodiment, each method can further include combining at least one type of polymer monomer together and reacting the monomer under polymerization conditions suited to produce the desired linear oligomer. Methods for producing linear oligomers from a variety of polymer monomers are known in the field and include use of conventional melt-processing and extrusion techniques. Preferred polymer monomers generally have a molecular weight of from between about 100 to about 350 although polymer monomers lower or higher than this range may be suited for particular applications of this invention.

10       The invention provides several important advantages. For example, and as discussed, preferred use of the methods facilitates effective melt-processing with good flow characteristics at low temperatures of about 200 °C. At these low temperatures, integrity of some of all of the nanocomposites can be maintained. In addition, the methods generally enhance dispersal of the layered silicates within polymer matrices at relatively low polymer melting temperatures, ie., about 200 °C. Also, use of toxic or potentially toxic solvents is significantly avoided. These advantages positively impact methods for making the nanocomposites and improve many features of the polymer system.

20       As discussed, preferred linear oligomers suitable for the macrocyclic method generally undergo ring-opening and linear polymerization. As will be shown in the discussion and examples which follow, this feature of the invention provides several advantages. For example, it has been found that opening the macrocycle in accord with this invention typically reduces or eliminates polymer void formation. Without wishing to be bound to theory, it is believed that the present methods decrease or substantially eliminate undesired condensate byproduct formation, thereby reducing the voids. This feature of the invention significantly improves several high performance characteristics of the nanocomposites including hardness and ablative properties.

25       In particular, the lower processing temperatures achievable by use of this invention help to preserve many types of layered silicates from thermal degradation.

**BRIEF DESCRIPTION OF THE DRAWINGS**

Figure 1 is a schematic drawing showing macrocyclic polymerization according to the invention. A linear oligomer is "grown" in dilute solution to favor intramolecular reaction and production of a macrocyclic oligomer. This macrocycle is thermally broken ("ring-opened") with heat and catalyst, thereby  
5 converting it to a high molecular weight polymer. Shown also in the figure is production of the polymer by conventional intermolecular polymerization.

Figure 2 is a drawing showing illustrative linear oligomers for use in the macrocyclic method. For clarity, the oligomers are arranged into groups  
10 designated as "G". Abbreviations are as follows 6F=6F-bisphenyl; DPE=diphenylether, BP=biphenyl, PH= phthalazinone; FL-bisphenylfluorene. The paranthetic formula shows illustrative macrocyclic oligomers made by using bis(fluorophenyl)phenyl phosphine oxide (BFPPO).

Figure 3 is a drawing showing an illustrative macrocyclic oligomer formed  
15 by reacting phenyl phosphine oxide (BFPPO) and bisphenol 6F. This macrocycle is a single large ring member.

Figure 4 is a drawing showing an X-ray diffraction (XRD) pattern of a nanocomposite made from a layered silicate material (10% Dodecyl ORMLAS) and 6F-PAEPPO.

20 Figure 5 is a schematic drawing showing fabrication of a high use-temperature nanocomposite using the polycyclic method with phenyl formaldehyde oligomer. Reaction of this linear oligomer forms a polycyclic oligomer having ring members made from reaction with aryl dichlorophosphite. The polycyclic oligomer is combined with low melt viscosity polycarbonate under  
25 cross-linking conditions to produce the nanocomposite. The resulting nanocomposite is illustrated as a strong and substantially void-free crosslinked network.

Figure 6 is a graph showing an X-ray Diffraction (XRD) pattern for aluminooctylsilsesquioxane ( $C_8$ ORMLAS).

30 Figure 7 is a graph showing an XRD pattern for aluminododecylsilsesquioxane ( $C_{12}$ ORMLAS).

Figure 8 is a graph showing an XRD pattern for

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aluminooctadecylsilsesquioxane (C<sub>18</sub>ORMLAS).

Figure 9 is TEM image of Al-Octadecyl Silsesquioxane (C<sub>18</sub>ORMLAS)/Ultem Nanocomposite.

## 5 DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

As discussed, the present invention features nanocomposites and methods for making the same that involve combining at least one type of cyclic oligomer with at least one type of layered silicate material under conditions which include making the nanocomposite. The methods more specifically include macrocyclic and polycyclic synthetic routes that significantly reduce polymer void, enhance melt-processing and improving flow characteristics while avoiding use of solvent and/or high temperature melting manipulations in most instances. The methods are generally flexible and can be used with a wide variety of cyclic oligomers and layered silicates. Nanocomposites produced by the method have a variety of high performance characteristics including good hardness and ablative properties.

Preferred macrocyclic methods in accord with this invention are compatible with use of a wide variety of suitable oligomers. Preferred are macrocyclic oligomers that have a melting temperature of from between about 150°C to about 250°C. Additionally preferred macrocyclic oligomers have a glass transition temperature of from between about 250°C to about 300°C. Other preferred macrocyclic oligomers have a thermal decomposition temperature of at least about 450°C.

The polymer produced in the macrocyclic method can have one or a combination of desired properties depending on intended use and the particular processing method selected. A preferred polymer has a glass transition temperature of from between about 175°C to about 275°C. Also preferred is a polymer having a viscosity of from between about 0.2 dL/g to about 1 dL/g at a temperature of from between about 250°C to about 350°C.

In a particular embodiment of the macrocyclic method, the combining step is conducted at a temperature of from between about 150°C to about 250°C. Sometimes this temperature range will be referred to as a "low" temperature or

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"low" temperature of processing. A more preferred low temperature is about 200°C. As discussed, the invention provides for low temperature processing and particularly low temperature polymer melting. In contrast, prior methods for making nanocomposites employ substantially higher processing temperatures for melting which can damage or destroy components such as the layered silicates present in the admixture.

In another particular embodiment of the macrocyclic method, the macrocycle and more particularly the ring member is opened at a temperature of from between about 275°C to about 450°C. Sometimes that temperature range will be referred to as a "ring-opening" temperature or related phrase. A ring-opening temperature of about 300°C to about 350°C will often be preferred for many applications. Methods for identifying and quantifying thermal stability of the ring member are known in the field and include determining whether a high molecular weight polymer has been produced at or near the ring-opening temperature. By the term "high molecular weight polymer" is meant a polymer having a molecular weight at least about 7000 with above about 10,000 to about 15,000 being preferred for most nanocomposites.

In another particular embodiment of the macrocyclic method, the polymerization step is conducted at a temperature of from between about 275°C to about 425°C. In some instances, this temperature will be referenced as a linear polymerization temperature. A preferred linear polymerization is between from about 300°C to about 375°C.

As discussed, preferred macrocyclic methods for making the nanocomposite include use of a suitable buffer. A preferred buffer is a carbonate salt such as a sodium or potassium carbonate salt. A preferred solvent in the method is dimethylformamide (DMF) or tetrahydrofuran (THF) although for some applications other solvents may be just as suitable.

As also discussed, the macrocyclic method preferably includes use of a suitable catalyst to help form the macrocycle. In one embodiment, the cyclization step of the method further comprises adding a suitable catalyst which catalyst may be a salt of fluoride, bisphenate, stearate or phthalamide. A particularly preferred

salt is CsF, potassium bisphenate, stearyl amine, or potassium phthalimide.

By the term "salt" is meant an ionic molecule that consists essentially of a desired anion and counter ion. By the term "counter-ion" is meant a positively charged atom or molecule (cation) that is capable of forming an ionic bond in the salt. Illustrative counter-ions include halides such as lithium, sodium, potassium, rubidium, and cesium; metal such as copper, zinc and iron; amine, and ammonium.

A preferred linear oligomer for use in the macrocycle method has a molecular weight of from between about 500 to about 6000, preferably from between about 1400 to about 5000 and more preferably about 2000. More particular linear oligomers and methods for making same are described below and include a wide variety of suitable carbonates, sulfonates, phenylene sulfides, axylene ethers and arylene ether imides. Methods for making and using these particular compounds have been described. See, e.g., Brunell, D.J. and Shannon, T. G. (1991) *Macromolecules* 24: 3035; Xie., D. and Gibson, H.W. (1994) *Polym. Prepr.* 35: 401; Ding, Y. and Hay, A.S. *Macromolecules* 29: 4811; Wang et al. (1996) *J. Poly. Sci. Part A: Polym. Chem.* 34: 2135; Takekoshi, T. and Terry, J.M. (1997) *Polym. Prepr.* 38: 70.

See also the following references for additional disclosure relating to making and using macrocycles suitable for use with this invention: U.S. Patent No. 5,264,520 to Mullins & Woo entitled "*Polymerization of Cyclic Poly(Aryl Ether) Oligomers*"; U.S. Patent No. 5,110,893 to Fukuyama entitled "*Preparation and Polymerization of Cyclic Aromatic Ketones*"; and U.S. Patent No. 5,405,956 to Hay & Chan entitled "*Cyclic Oligomers for Production of Linear Polyketones, Polyphthalazines and Polyisoquinolines*"; the disclosures of which patents are incorporated herein by reference.

In embodiments of the method in which use of a polymer monomer is desirable, that monomer will have a preferred molecular weight of from between about 75 to about 400 with between from about 100 to about 350 being generally preferred. More preferred is a polymer monomer selected from the following group: 6F-bisphenyl (6F); diphenylether (DPE), biphenyl (BP), phthalazinone (PH); bisphenylfluorene (FL); and bis(fluorophenyl) phenyl phosphine oxide



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(BFPPPO). See Figure 2 for drawings of these preferred monomers.

As also mentioned, the polycyclic methods of this invention are flexible and can be used with one or a combination of suitable linear oligomers. In one particular embodiment, the linear oligomer is a phenyl formaldehyde oligomer as  
5 shown in Figure 5 and discussed below in Example 5.

Additionally specific linear oligomers for use in the macrocyclic or polycyclic synthetic routes include those oligomers having between from about 1 to about 10 optionally substituted aryl rings with between from about 1 to about 4 to about 5 of such aryl rings being preferred from many applications. Choice of a  
10 particular polymer precursor will be guided by several factors including intended use of the nanocomposite.

Illustrative layered silicates suitable for use with this invention have been disclosed in a U.S. Provisional Application USSN 60/152,515 filed on September 2, 1999 and entitled "High Temperature Use Nanocomposites". The U.S.  
15 Provisional Application USSN 60/152,515 is sometimes referred to herein as "'515 provisional application" and its disclosure is hereby incorporated by reference.

The terms "layered silicates", "layered inorganic silicates", "layered silicate materials" and the like are often used interchangeably in the present  
20 application and in the '515 provisional application.

In particular, the '515 provisional application discloses a wide spectrum of suitable inorganic layered silicates and specifically synthetic and natural clays. Such materials are readily used in accord with the methods of this invention.

For example, preferred natural clays are typically phyllosilicates and  
25 related materials. Illustrative materials are smectite clay minerals such as montmorillonite, nontronite, sepiolite, atapulgite, beidellite, volkonskoite, hectorite, saponite, sauconite, magadiite, and kenyaite; vermiculite; and the like. Other useful layered materials include illite minerals such as ledikite and admixtures of illites with the clay minerals. Other useful layered materials,  
30 particularly useful with anionic polymers, are the layered double hydroxides. See e.g., W. T. Reichle, *J. Catal.*, 94 (12985) 547). Many of these clays have positively charged layers and exchangeable anions in the interlayer spaces.

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Additional phyllosilicates include the 2:1 type having a negative charge on the layers ranging from about 0.25 to about 0.9 charges per formula unit and a commensurate number of exchangeable cations in the interlayer spaces. More preferred layered materials are smectite clay minerals such as montmorillonite, nontronite, beidellite, bolkonskoite, hectorite, saponite, sauconite, sepiolite, 5 fluorohectorite, atapulgite, laponite magadiite, and kenyaite. Generally preferred smectites include aluminosilicates, magnesiosilicates as well as mixtures thereof.

See also U.S. Pat. No. 5,385,776 for other clay minerals suitable for use 10 with this invention.

The amount of clay mineral used in a nanocomposite of this invention will vary depending on intended use and particularly by the performance characteristics desired. For example, an amount of clay mineral (or combination of clay minerals) less than about 0.5% by weight of the matrix will be useful for 15 many applications. For other applications however, the amount of clay mineral may approach several parts per million or less. Preferably the amount of a particular clay mineral in a silicate composition will be from between about 0.1% by weight to about 10% by weight with between from about 0.1% by weight to about 0.5% by weight of the matrix being preferred for many applications.

20 More particularly preferred is clay levels from about ppm level up to about 10% clay in the resulting polymer matrix of the nanocomposite.

Also provided by the disclosure of the '515 provisional application are methods for making and using a wide variety of synthetic layered silicate materials and particularly ORganically Modified Layered ALuminosilicateS (hereinafter "ORMLAS"). More particular layered silicate materials include 25 between from one to about 5 of the inorganic layered silicates, preferably one of same, and between from one to about 5 ORMLAS, preferably one of same. Thus it is an objective of this invention to provide nanocomposites and methods for making same that can include a mixture of silicate types including those with one type of inorganic layered silicate type, e.g., a natural clay and one type of 30 ORMLAS.

Unless stated otherwise, reference herein to "ORMLAS" is meant to

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encompass one type of organically modified layered aluminosilicates.

Further provided by the disclosure of the '515 provisional application are several methods for making ORMLAS that generally involve combining specific layered silicates and the organic compatibilizing agent in a single chemical compound. This aspect of the invention provided by the '515 provisional application renders the ORMLAS thermally stable, exceptionally organophilic and compatible with a range of suitable polymer materials. As discussed in the '515 provisional application in detail, the ORMLAS and ORMLAS-related compositions are believed to include some of the most thermally stable silicate-organic interfaces known in the field.

By the term "ORMLAS-related" composition is meant ORMLAS plus at least one inorganic layered silicate as provided herein.

See Example 1 below describing a preferred method of making and using ORMLAS. See also the '515 provisional application for additional disclosure regarding ORMLAS.

Unless otherwise stated the amount of ORMLAS in a nanocomposite of this invention will approximate the amounts stated above for clay minerals.

As discussed in the '515 provisional application, ORMLAS and related materials can generally provide favorable interfacial chemistry as well as a thermally stable interface. These important features are harnessed by that invention and particularly by the processing steps disclosed therein. For example, the ability to melt-flow the cyclic oligomers described in the present application at low temperatures facilitates molecular dispersion of ORMLAS layers as a suitably low-viscosity melt at temperatures which are lower than would be necessary for melt-processing with other polymer systems. Further protection is thus provided by reducing the exposure of the organic chains of ORMLAS materials to thermo-oxidative damage during higher-temperature melt-processing of high use-temperature thermoplastic polymer systems.

Illustrative ORMLAS for use with the invention include  $C_{12}$  ORMLAS,  $C_{18}$  ORMLAS, as well as other specific ORMLAS disclosed in the Examples and in the '515 provisional application.

As discussed, the invention also includes highly useful polycyclic methods

for making a desired nanocomposite. In one embodiment of the polycyclic method, the melting step is preferably performed at a temperature of between about 175°C to about 275°C. In another embodiment of the method, the cross-linking step is performed at a temperature of from between about 300°C to about  
5 450°C.

The term "aryl" as used herein, and unless otherwise specified, refers to phenyl or substituted phenyl, wherein the substituent is halo, hydroxy, alkaryl, haloalkyl, haloalkenyl, haloalkynyl, lower alkoxy or lower alkyl.

The term "halo" is used in its conventional sense to refer to a chloro,  
10 bromo, fluoro or iodo substituent. The terms "haloalkyl," "haloalkenyl" or "haloalkynyl" (or "halogenated alkyl," "halogenated alkenyl," or "halogenated alkynyl") refers to an alkyl, alkenyl or alkynyl group, respectively, in which at least one of the hydrogen atoms in the group has been replaced with a halogen atom.

The terms "heterocycle" or "heteroaromatic," as used herein, and unless otherwise specified, refer to an aromatic moiety that includes at least one sulfur, oxygen or nitrogen atom in the aromatic ring. Such moieties include, but are not limited to, pyrrol, furyl, pyridyl, 2,4-thiadiazolyl, pyrimidyl, thienyl, isothiazolyl, imidazolyl, tetrazolyl, pyrazinyl, pyrimidyl, quinolyl, isoquinolyl, benzothienyl,  
20 isobenzofuryl, pyrazolyl, indolyl, purinyl, carbazolyl, benzimidazolyl and isoxazolyl.

The term "aralkyl" refers to an aryl group with an alkyl substituent.

The term "alkaryl" refers to an alkyl group that has an aryl substituent.

The term "alkyl" as used herein, unless otherwise specified, refers to a  
25 saturated straight chain, branched or cyclic hydrocarbon group of 1 to 10 carbon atoms, such as methyl, ethyl, *n*-propyl, isopropyl, *n*-butyl, isobutyl, *t*-butyl, pentyl, cyclopentyl, isopentyl, neopentyl, hexyl, isohexyl, cyclohexyl, 3-methylpentyl, 2,2-dimethylbutyl, and 2,3-dimethylbutyl. The term "lower alkyl" intends an alkyl group of one to six carbon atoms, and includes, for example,  
30 methyl, ethyl, *n*-propyl, isopropyl, *n*-butyl, isobutyl, *t*-butyl, pentyl, cyclopentyl, isopentyl, neopentyl, hexyl, isohexyl, cyclohexyl, 3-methylpentyl, 2,2-dimethylbutyl, and 2,3-dimethylbutyl.

The term "alkenyl" as used herein, unless otherwise specified, refers to a branched, unbranched or cyclic (in the case of C<sub>3</sub> and C<sub>6</sub>) hydrocarbon group of 2 to 10 carbon atoms containing at least one double bond, such as ethenyl, vinyl, allyl, octenyl, decenyl, and the like. The term "lower alkenyl" intends an alkenyl group of two to six carbon atoms, and specifically includes vinyl and allyl.

The term "alkynyl" as used herein, unless otherwise specified, refers to a branched or unbranched hydrocarbon group of 2 to 10 carbon atoms containing at least one triple bond, such as acetylenyl, ethynyl, *n*-propynyl, isopropynyl, *n*-butynyl, isobutynyl, *t*-butynyl, octynyl, decynyl and the like. The term "lower alkynyl" intends an alkynyl group of two to six carbon atoms, and includes, for example, acetylenyl and propynyl.

More specific polymers in accord with this invention include chemically optimized and thermally stable inorganic layered silicate systems. These precursors are sometimes referred to herein as "polymer matrices" and include a series of polytherimides (Ultem 1000® to Ultem 6000®, both made by General Electric); thermoplastic polyimides (Aurum PL450® with a T<sub>g</sub> of 260 °C, both made by Mitsui Toatsu); liquid crystal polymers (made by Vectra®); macrocyclic oligomers of PolyAryleneEther matrix; and polycyclic carbonate. The first of three of the above five matrices are thermoplastic polymers, used for nanocomposite fabrication via solvent-free direct melt processing.

See also Kaplan, W. ed in *Modern Plastics Encyclopedia* (1999) (McGraw-Hill Companies, NY) for more detailed information relating to these and other suitable polymers; the disclosure of which is hereby incorporated by reference.

An acceptable low melt viscosity polymer for use with this invention melts at a temperature of from between about 200°C to about 250°C with suitable melt viscosity at that temperature. Additionally preferred is a low melt viscosity polymer that can be cross-linked to another polymer in the melt phase. More preferred is low melt viscosity polycarbonate although other low melt viscosity polymers may be well-suited for other applications of this invention.

In preferred embodiments, the present method is an environmentally-friendly, simple one-step technique that yields nanocomposites from physical

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mixtures of the polymer resin and the inorganic phase. The invented method permits the fabrication of nanocomposites with excellent nanoscale dispersion of the inorganic layers within the polymer matrix. The invented method especially permits the fabrication of nanocomposites from polyetherimides (Ultem®) and  
5 6F-PAEPPC polymers.

By the term "cyclic oligomer" or related term is meant a polymer precursor which as has a feature at least one ring member. More specific cyclic oligomers include those linear oligomers described above and in the examples which follow.

By the term "oligomer" unless otherwise provided, is meant a compound  
10 capable of being polymerized and having at least two and preferably between from about two to about ten repeating chemical units with between from about two to about four of such units being preferred in most instances.

A nanocomposite made by the macrocyclic or polycyclic methods of this invention have several desirable properties. For example, the Si-C bond typically  
15 provides remarkable interfacial thermal stability as the surrounding polymer matrix prevents the access of oxygen to the layers. An extremely thermally stable interface for high-temperature use of the nanocomposites is thus provided. Several studies have shown the remarkable stability of Si-C bonds under inert atmospheres and Si-C bonds are believed to be so thermally stable that  
20 organically-modified silicate precursors are used to synthesize SiC by pyrolysis under inert atmospheres up to temperatures over 1500 °C. In contrast, although the present methods can be used to create nanocomposites at lower temperatures from traditional clays with ion-exchanged organic surfactants, the interface degrades during use at high temperatures with accompanying degradation in  
25 properties.

Macrocycles made from suitable carbonates, sulfonates, phenylene sulfides, axylene ethers and arylene ether imides referenced above have been prepared by modification of published procedures for making linear polymers. That is, the procedures were modified to favor macrocycle formation by what is  
30 known as "head to tail" polymerization. Very dilute reaction conditions typically facilitate head-to-tail intramolecular reaction rather than chain forming intermolecular reactions. The resulting oligomers have a very low melt flow for

ease in processing. In the presence of a suitable catalyst, they ring open to form the desired linear polymer. The part may then be fabricated without using solvent or high pressure thermoforming techniques.

5 Additionally, polyetherimide (Ultem®) and 6F-PAEPPC polymers can be employed to make a high-temperature, high performance nanocomposite in accord with this invention. The invented method significantly enhances the processibility of nanocomposites from high use-temperature, high performance matrices by permitting nanocomposite fabrication in low-viscosity melts at low temperatures. In this embodiment, the reaction is followed by a thermally-activated  
10 polymerization step with no volatiles. The low viscosity of the melt promotes a nanoscale dispersion of the layers and provides superior properties. Significantly, the lower processing temperatures protect the organic groups on the layered silicates from thermo-oxidative damage during fabrication.

An important advantage of the macrocyclic and polycyclic approaches  
15 of this invention are that the cyclic oligomers allow melt processing with good flow characteristics at relatively low temperatures. The layered silicate materials can be easily dispersed in the matrix at these temperatures. This allows solvent-free melt processing and component-fabrication at 200°C. With respect to the macrocyclic method, ring opening polymerization is then carried out by  
20 heating the finished component at a slightly elevated temperature (350°C), thus yielding a high-performance polymer system. Inexpensive cyclic oligomers thus provide a convenient processing route and a high performance polymer system.

"Optional" or "optionally" means that the subsequently described  
25 circumstance may or may not occur, so that the description includes instances where the circumstance occurs and instances where it does not. For example, the phrase "optionally substituted" means that a non-hydrogen substituent may or may not be present, and, thus, the description includes structures wherein a non-hydrogen substituent is present and structures wherein a non-hydrogen substituent is not present.

30 "Layered Material" shall mean an inorganic material, such as a smectite clay mineral, that is in the form of a plurality of adjacent, bound layers and has a thickness, for each layer, as specified herein.

"Platelets" shall mean individual layers of the Layered Material.

"Intercalate" or "Intercalated" shall mean a Layered Material that includes polymer material disposed between adjacent platelets of the Layered Material to increase the interlayer spacing between the adjacent platelets to at least about 5 Å.

5 "Intercalation" shall mean a process for forming an Intercalate.

"Intercalant Polymer" or "Intercalant" shall mean an oligomer or polymer that is sorbed between Platelets of the Layered Material and complexes with the platelet surfaces to form an Intercalate.

10 "Intercalating Carrier" shall mean a carrier comprising water with or without an organic solvent used together with an Intercalant Polymer to form an Intercalating Composition capable of achieving Intercalation of the Layered Material.

"Intercalating Composition" shall mean a composition comprising an Intercalant Polymer, an Intercalating Carrier for the Intercalant Polymer, and a  
15 Layered Material.

"Exfoliate" or "Exfoliated" shall mean individual platelets of an Intercalated Layered Material so that adjacent platelets of the Intercalated Layered Material can be dispersed individually throughout a matrix polymer; or throughout a carrier material, such as water, an alcohol or glycol, or any other organic solvent.

20 "Exfoliation" shall mean a process for forming an Exfoliate from an Intercalate.

"Nanocomposite" shall mean an oligomer, polymer or copolymer having dispersed therein a plurality of individual platelets obtained from an Exfoliated, Intercalated Layered Material.

25 "Matrix Polymer" shall mean a thermoplastic or thermosetting polymer in which the Intercalate and/or Exfoliate is dispersed to form a Nanocomposite.

By the term "linear polymer intermediate" is meant a high molecular weight polymer precursor formed by ring-opening of a suitable macrocycle. Preferred molecular weight of the linear polymer intermediate will generally vary  
30 depending on the macrocycle selected for use. Presence of the linear polymer intermediate can be detected by one or a combination of different strategies including identification of high molecular weight polymer preferably formed by



linear polymerization of the intermediate.

While the invention has been described with reference to specific embodiments, modifications and variations of the invention may be constructed without departing from the scope of the invention.

5

#### Example 1- ORMLAS Syntheses

The ORMLAS synthetic layered silicates were prepared by our standard self-assembly route by the titration of  $\text{AlCl}_3$  and the organotrialkoxysilane in EtOH with NaOH.

Three ORMLAS were prepared by the following standard route by the titration of  $\text{AlCl}_3$  and the organotrialkoxysilane in ethanol with NaOH. The XRD patterns for the alumino- *octyl*, *dodecyl*, and *octadecyl* silsesquioxanes are shown in Figures 6, 7, and 8 respectively. The patterns clearly show an increase in d-spacing (25.1, 37.5, 53.5 Å respectively), as well as improved crystallinity, as the organic chain length is increased. Thermal analyses as described below showed the effect of chain length on the thermal stability of these materials. Previous TGA experiments on the dodecyl analogue have shown that the layered structure is intact up to temperatures of 350 °C in either air or inert atmosphere. An increase in organic chain length is likely to lead to a better dispersion of the silicate layers, and to a more delaminated nanocomposite. The increase in hydrophobicity will also yield better interactions with hydrophobic polymers.

A particular goal of these studies was to increase the aspect ratio of the layered silicates by increasing the length of the individual silicate layers of the ORMLAS materials. Impact on the effect of plate size (aspect ratio) on gas barrier and thermo-mechanical properties of the nanocomposites can also be addressed.

A preferred method of making the ORMLAS was as follows: An aqueous solution of NaOH (0.1M) was added dropwise with vigorous stirring to  $\text{AlCl}_3$  (6.04g, 25mmol) and dodecyltriethoxy silane (16.63g, 50mmol) in ethanol (250ml) to a pH of 5.5 at room temperature. A white precipitate that formed was allowed to age in solution for 16 hours. Then the solid was filtered, washed with

water, and dried at 90°C for 6 hours.

More particular details about the mixed ORMLAS synthesis is as follows:

The synthesis for the mixed ORMLAS materials was the same as that for the standard ORMLAS except that a mixture of the organosilanes were added. For example, for a ORMLAS material with a 1:1 ratio of methyl:dodecyl, a 1:1 molar ratio of methyltriethoxysilane and dodecyltriethoxy silane were used in the synthesis.

For additional disclosure relating to making the ORMLAS see Ukrainczyk, L. et al. Materials Research Society Symposium on *'Nanocomposites of Layered and Mesoporous Materials'*, Boston, MA, December, 1996; Fukushima, Y. and M. Tani, *J. Chem. Soc. Chem. Commun.* pg. 241 (1995); and Ukrainczyk, et al. *J. Phys. Chem. B.* 101: 531 (1997).

As discussed, Alumino n-Dodecylsilsesquioxane, Alumino n-Octadecylsilsesquioxane, and Alumino n-Phenylsilsesquioxane were synthesized using the described template sol-gel approach. These ORMLAS materials are layered alumino-silicate structures having dodecyl, octadecyl and phenyl organic modifying groups, respectively in the interlayers, connected to the Si atom through Si-C bonds. X-ray diffraction patterns of the three ORMLAS materials are shown in Figures 6-8. Alumino-Dodecylsilsesquioxane displays the most ordered structure followed by Alumino-Octadecylsilsesquioxane and Alumino-Phenylsilsesquioxane respectively. Very sharp peaks reflecting a high degree of order in the layered structure are obtained for Alumino-Dodecylsilsesquioxane. A layer spacing of up to 3.9 nm is obtained from the XRD pattern. Four orders of the basal reflections are observed. The lack of non-integer orders of basal spacing also implies an ordered lamellar structure. The Alumino-Phenylsilsesquioxane does not show an ordered structure. This observation is consistent with our experience with the nature of ordering in ORMLAS materials.

A Transmission Electron Micrograph clearly showing the layers in Alumino-Dodecylsilsesquioxane powder is displayed in Figure 9. The powders were dried in air at ~75°C, were dispersed in ethanol and placed on Cu grid for placing inside the microscope. The TEM picture was obtained at 120 kV, and at a

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magnification of 200K. The bar in the bottom right hand side represents 20 rim on the picture. Hence, an estimate of the layer spacings has easily been obtained. The layer spacing of (~ 4 nm) revealed in the micrograph matches that obtained from the XRD patterns.

5           The above-referenced ORMLAS synthetic methods have been improved. For example, it has been found that alumino - dodecylsilsesquioxane has consistently yielded the most well-ordered layered structure. Thus much standardization and streamlining effort has been applied to this organic modification.  $\text{AlCl}_3$  and Dodecyl triethoxysilane were used as sources for Al and  
10 Si respectively. Their electrostatic interactions were controlled by adjusting the pH using NaOH. Ethanol was used as the solvent. The synthesis process is simple and consistent, and yields layered structures reproducibly.

          Accordingly, the present invention also features methods for modifying spacing between the inorganic silicate layers of ORMLAS which method includes  
15 adjusting the pH of a solution comprising the ORMLAS under conditions that enable achievement of the desired spacing. As discussed, preferred d-spacing can be determined by TEM or other suitable technique.

          See the U.S. Provisional Application USSN 60/152,515 filed on September 2, 1999 and entitled "High Temperature Use Nanocomposites" for  
20 additional disclosure relating to making and using ORMLAS.

#### **Example 2- Production of Macrocyclic Oligomers and Use to Make Nanocomposite**

          As discussed above, the melting temperature of macrocyclic oligomers in  
25 accord with this invention are generally much lower than those of most polymers e.g., about 200°C compared to 300°C for polymer. This feature helps to make processing of polymer produced from the macrocycle much easier. A process termed 'curing' the macrocycle, i.e. ring opening and polymerization is used to make linear polymer at a temperature of about 350°C or so.

30           Briefly, macrocyclic oligomers were formed from chains grown in dilute solution such that the probability of one chain end reacting with its other end is much more likely than growing through the addition of another growing chain of

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oligomer unit (see Figure 1). A theoretical example of macrocycle synthesis is provided in Figure 3 for the reaction of bisphenol 6F and bis(fluorophenyl) phenyl phosphine oxide (BFPPPO).

More specifically, the macrocyclic materials were prepared by the following route. Stoichiometrically equivalent amounts of  
5 bis(4-fluorophenyl)phenyl phosphine oxide and a bisphenol containing one of the moieties G (see Figure 2) were dissolved in DMF resulting in a concentration of 0.1M. This solution was added to a refluxing solution of DMF/toluene  
10 (25:2 by volume) containing 1.8 equivalence of potassium carbonate. The initial volume of DMF in the refluxing solution was 2.5 times the volume of DMF monomer solution to be added. The addition was carried out over an 8 hour period accompanied by the azeotropic removal of water via a Dean-Stark trap. An additional 8 hours at reflux was utilized to complete the reaction. The  
15 macrocycles obtained from these reactions were amorphous materials exhibiting glass transition temperatures below 300°C and thermal decomposition temperatures exceeding 460°C under nitrogen. The cyclic nature of the oligomers was confirmed via comparison of MALDI-TOF mass spectra, <sup>13</sup>C and <sup>19</sup>F NMR, and GPC data of the reported materials with values obtained for the linear  
20 oligomers of the same repeat unit produced by intentionally offsetting the stoichiometry.

A ring opening polymerization of the biphenyl (BP) containing macrocycle in the presence of 5.2 molar % of potassium 4,4'-biphenate at 350°C for 45 minutes resulted in a linear polymer with an inherent viscosity of 0.48  
25 dL/g. This resultant polymer had a glass transition temperature of 245°C matching the literature value for the same linear polymer.

The macrocycle and corresponding linear polymer produced in this method can be used to make a wide variety of nanocomposites. Briefly, the macrocycle  
30 can be combined with at least one suitable layered silicate and reacted appropriately to form the nanocomposite.

More specific methods for making nanocomposite have been disclosed in

the U.S. Provisional Application USSN 60/152,515 filed on September 2, 1999 and entitled "High Temperature Use Nanocomposites". The methods disclosed in the '515 provisional application can be readily adapted so that macrocycle is preferably employed to make nanocomposite instead of the polymer material disclosed in that application.

Additional macrocycles have been made along lines of the specific method provided in Example 2. These macrocycles are schematically represented in Figure 2 and they have successfully combined with various natural and synthetic clays with good results.

#### **Example 3- Production of Additional Macrocyclic Oligomers**

As discussed above in Example 2, a wide variety of macrocycles have been made in accord with this invention.

In one series of experiments, macrocycle, clay, and catalyst (e.g., CsF) were ground together, sealed under nitrogen and heated to 300 °C. Since the macrocycle generally begins to react at about the same temperature it melts, it is possible that there may be incomplete dispersion. To improve this, the clay was dispersed in tetrahydrofuran (THF), and a solution of the macrocycle was added, resulting in a flocculation of the clay. This indicated that intercalation took place.

This was then filtered, dried, then cured at 300 °C. This macrocyclic oligomer approach is compatible with standard extrusion processes that will further aid in the dispersion of clay within the polymer matrix.

#### **Example 4- Production of Polycyclic Oligomer and Use to Make Nanocomposite**

A macrocycle was prepared from 6F-PAEPPC (see Figure 2) along lines provided in Examples 2-3 above. That macrocycle was used to prepare a polymer layered silicate nanocomposite.

More particularly, the the macrocycle (94% ), C<sub>12</sub> ORMLAS (5% by weight), and ring opening catalyst lithium stearate (1%) were melt processed in a twin screw extruder at 200-220°C. This resulted in an intercalated nanocomposite with interstitial macrocycle between the silicate sheets as evidenced by X-Ray

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Diffraction (XRD). The resultant material was heated at 350°C to ring-open the macrocycle and thus produce the linear polymer. The thermal properties of this polymer nanocomposite matched those of the synthesized linear polymer.

5     **Example 5- Production of Polycyclic Oligomer and Use to Make Nanocomposite**

A crosslinked polycarbonate layered silicate nanocomposite was prepared by a polycyclic route as shown in Figure 5. Briefly, a polycyclic phosphonate ester was prepared by reaction of an aryl dichlorophosphite with phenol formaldehyde oligomer. This polycyclic phosphonate (5%), low melt viscosity polycarbonate (89%), lithium stearate (1%), and C<sub>12</sub> ORMLAS (5%) were melt  
10     processed via twin screw extrusion at 200-240 °C.

The resultant nanocomposite displayed excellent dispersion of the silicate layers within the polymer matrix by XRD. This nanocomposite was then cured at 350°C to crosslink the polycarbonate to the phosphonate. Differential scanning  
15     calorimetry of this material showed a loss of the glass transition temperature of polycarbonate, indicating that the crosslink occurred.

**Example 6- Nanocomposite Compounding Methods**

As discussed above, nanocomposites of this invention can be made by  
20     using conventional extruder implementations. Such an extruder is preferably a single or twin screw extruder such as those generally known in the field. In situations in which a twin screw extruder is used, the preferred embodiment shall make use of a co-rotating twin screw extruder as follows.

The twin co-rotating extruder shall consist of screws with 3 distinct sets of  
25     element types including: a) conveying elements, b) kneading elements, c) mixing/dispersion elements. In particular, 5-30% of the length of each screw shall consist of kneading elements; 5-15% of the length of the screw shall consist of mixing/dispersion elements; and 55-90% of the length of the screw shall consist of conveying elements.

30     It is often important to maintain a carefully defined pressure profile inside the extruder. This pressure profile includes high pressure in the kneading section for a short duration, layered silicate shall be added at a low pressure area after the

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neat resin has been melted, the mixing section shall be at lower pressure than in the kneading section, the conveyance section shall be approximately three times longer than the kneading section.

5 More specifically, to make the nanocomposite, the screws shall exhibit a length over diameter ratio (L/D) of between 30-35 to 1. The screw speed shall operate between 50-166 RPM.

There are generally two preferred methods of feeding the materials to be compounded into the extruder, namely by premixing the plastic resin with the nanolayered silicate and by feeding the two separately.

10 In the cases in which the desired nanocomposite includes more than one desired linear oligomer or polymer monomer (or a combination thereof), the materials (two or more) may also be premixed or introduced along the length of the extruder.

For example, the linear oligomer and the layered silicate shall be  
15 gravimetrically fed using a starve feeding methodology. Starve feeding introduces the material to be mixed using a controlled rate system. Use of starve feeding is essential to controlled mixing of the two components. The layered silicate shall be fed approximately 50% along the length of the extruder in order to allow the neat resin to reach its melting point.

20 One good way of feeding involves first feeding the thermoplastic resin in powder or pellet form. The extruder shall be preheated to a temperature set at 99%-110% of the melting point of the neat resin. The neat resin shall be at 99%-110% of its melting point at the point of intercalation or exfoliation. Such temperature profile shall be maintained during the mixing (compounding).

25 The exiting compounded (resin plus layered silicate) resin shall have a temperature of 102-110% of the melting point of the neat resin. In order to obtain compounded material with optimum properties, it is essential to extract entrapped volatiles in gaseous form within the last 10% of the length of the extruder.

30 The exiting compounded shall go through a mold which shall be able to impart certain geometric configuration on the thermoplastic compound. Such geometry may be in the form of a rod, film, sheet, or other complex shapes such as blow molded or extrusion blow molded article of manufacture.

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For applications in which an article of manufacture is to be made from the nanocomposite, that article exiting the extruder shall be quenched to a temperature of 10-100°C using liquid (such as water) or gaseous material (such as nitrogen or air).

- 5        More specific disclosure relating to preferred extrusion methods can be found in the U.S. Provisional Application USSN 60/152,515 filed on September 2, 1999 and entitled "High Temperature Use Nanocomposites".

It will be understood that the information provided in this example and in the '515 provisional application can be readily modified to suit an intended result.

- 10      For example it will be helpful in some situations to optimize pressure, heating and mixing profiles within a selected extruder implementation to facilitate a particular performance characteristic. Such optimization is within the skill of those and this field and will not require undue experimentation to achieve.

- 15      All references disclosed in this application are incorporated herein by reference.

While the invention has been described with reference to specific embodiments, modifications and variations of the invention may be constructed without departing from the scope of the invention, which is defined in the following claims.



What is claimed is:

1. A method of making a nanocomposite, the method comprising the steps of:
  - 5 a) cyclizing at least one type of linear oligomer under conditions that form at least one type of macrocyclic oligomer with a ring member,
  - b) combining the macrocyclic oligomer with at least one type of layered silicate to make an admixture,
  - c) opening the ring member to make a linear polymer intermediate,
  - 10 d) polymerizing the intermediate to make a polymer; and
  - e) producing the nanocomposite from the admixture.
2. The method of claim 1, wherein the method further comprises making the linear oligomer by polymerizing at least one type of polymer monomer.
- 15 3. The method of claim 1, wherein the macrocyclic oligomer has a melting temperature of from between about 150°C to about 250°C.
4. The method of claim 3, wherein the macrocyclic oligomer has a glass transition temperature of from between about 250°C to about 300°C.
- 20 5. The method of claim 4, wherein the macrocyclic oligomer has a thermal decomposition temperature of at least about 450°C.
6. The method of claim 1, wherein the polymer has a glass transition temperature of from between about 175°C to about 275°C.
7. The method of claim 6, wherein the polymer has a viscosity of  
25 from between about 0.2 dL/g to about 1 dL/g at a temperature of from between about 250°C to about 350°C.
8. The method of claim 1, wherein the combining step is conducted at a temperature of from between about 150°C to about 250°C.
9. The method of claim 1, wherein the ring member is opened at a  
30 temperature of from between about 275°C to about 450°C.
10. The method of claim 1, wherein the polymerization step is

conducted at a temperature of from between about 275°C to about 425°C.

11. The method of claim 1, wherein the cyclization step further comprises diluting the linear oligomer (or mixture thereof) in a suitable solvent, wherein the ratio of the solvent to the linear oligomer is from between about 1.5 to about 25 (v/v).

12. The method of claim 11, wherein the cyclization step further comprises including a buffer, wherein the ratio of the buffer to the solvent is between from about 1.5 to about 5 (v/v).

13. The method of claim 12, wherein the buffer is a carbonate salt.

14. The method of claim 11, wherein the solvent is dimethylformamide (DMF) or tetrahydrofuran (THF).

15. The method of claim 11, wherein the cyclization step further comprises adding at least one suitable catalyst.

16. The method of claim 15, wherein the catalyst is a salt of fluoride, bisphenate, stearate or phthalamide.

17. The method of claim 1, wherein the linear oligomer comprises at least one optionally substituted aryl group.

18. The method of claim 17, wherein the linear oligomer further comprises at least one optionally substituted heterocyclic group.

19. The method of claim 1, wherein the linear oligomer has a molecular weight of from between about 500 to about 5000.

20. The method of claim 2, wherein the polymer monomer has molecular weight of from between about 100 to about 350.

21. The method of claim 19, wherein the macrocyclic oligomer has a molecular weight of from between about 2 to about 25 times the molecular weight of the linear oligomer.

22. The method of claim 1, wherein the ring member of the macrocyclic oligomer comprises from between about 2 to about 10 linear oligomers.

23. The method of claim 22, wherein the macrocyclic oligomer comprises a PEI, polyimide, polysulfone, or polycarbonate monomer.

24. The method of claim 1, wherein the layered silicate is ORMLAS or

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a natural clay.

25. The method of claim 24, wherein the ORMLAS is C<sub>8</sub>, C<sub>12</sub> or C<sub>18</sub> ORMLAS.

26. The method of claim 1, wherein the polymer is intercalated or  
5 exfoliated within layers of the silicate.

27. The method of claim 26, wherein the nanocomposite exhibits a d-spacing of at least about 18 Angstroms as determined by X-ray diffraction (XRD).

28. The method of claim 2, wherein the polymer monomer is selected from the following group: 6F-bisphenyl (6F); diphenylether (DPE), biphenyl  
10 (BP), phthalazinone (PH); bisphenylfluorene (FL); and bis(fluorophenyl) phenyl phosphine oxide (BFPPPO).

29. The method of claim 1, wherein the method is performed in an extruder.

30. The method of claim 29, wherein the nanocomposite is produced  
15 by outputting the admixture from the extruder.

31. A method of making a nanocomposite, the method comprising the steps of:

- a) making at least one polycyclic oligomer from at least one linear oligomer,
- 20 b) combining the polycyclic oligomer with at least one low melt viscosity polymer and at least one inorganic layered silicate to make an admixture,
- c) melting the polycyclic oligomer and the low melt viscosity polymer in the admixture,
- d) cross-linking the polycyclic oligomer and the low melt viscosity  
25 polymer; and
- e) producing the nanocomposite from the admixture.

32. The method of claim 31, wherein the method further comprises making the linear oligomer by polymerizing at least one type of polymer monomer.

30 33. The method of claim 32, wherein the polycyclic oligomer is made by combining the linear oligomer with at least one suitable phosphite having the

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following general formula:  $X_1-(P=O)-X_2-R$ ; wherein each of  $X_1$  and  $X_2$  is selected individually from the following group: F, Cl, and Br, and R is an optionally substituted aryl or alkyl group.

34. The method of claim 31, wherein the melting step is performed at a temperature of between about 175°C to about 275°C.

35. The method of claim 31, wherein the cross-linking step is performed at a temperature of from between about 300°C to about 450°C.

36. The method of claim 31, wherein the linear oligomer comprises at least one optionally substituted aryl group.

37. The method of claim 35, wherein the linear oligomer further comprises at least one optionally substituted heterocyclic group.

38. The method of claim 31, wherein the linear oligomer has a molecular weight of from between about 500 to about 5000.

39. The method of claim 32, wherein the polymer monomer has molecular weight of from between about 100 to about 350.

40. The method of claim 38, wherein the linear oligomer is a phenyl formaldehyde oligomer.

41. The method of claim 31, wherein the polycyclic oligomer has a molecular weight of from between about 500 to about 5500.

42. The method of claim 31, wherein the layered silicate is at least one of ORMLAS or a natural clay.

43. The method of claim 40, wherein the ORMLAS is  $C_8$ ,  $C_{12}$  or  $C_{18}$  ORMLAS.

44. The method of claim 31, wherein the cross-linking step produces a polymer that is intercalated or exfoliated within layers of the silicate.

45. The method of claim 44, wherein the nanocomposite exhibits a d-spacing of at least about 18 Angstroms as determined by X-ray diffraction (XRD).

46. The method of claim 31, wherein the method is essentially performed in an extruder.

47. The method of claim 46, wherein the nanocomposite is produced by outputting the admixture from the extruder.

48. A nanocomposite produced by the method of claim 1 or 31.

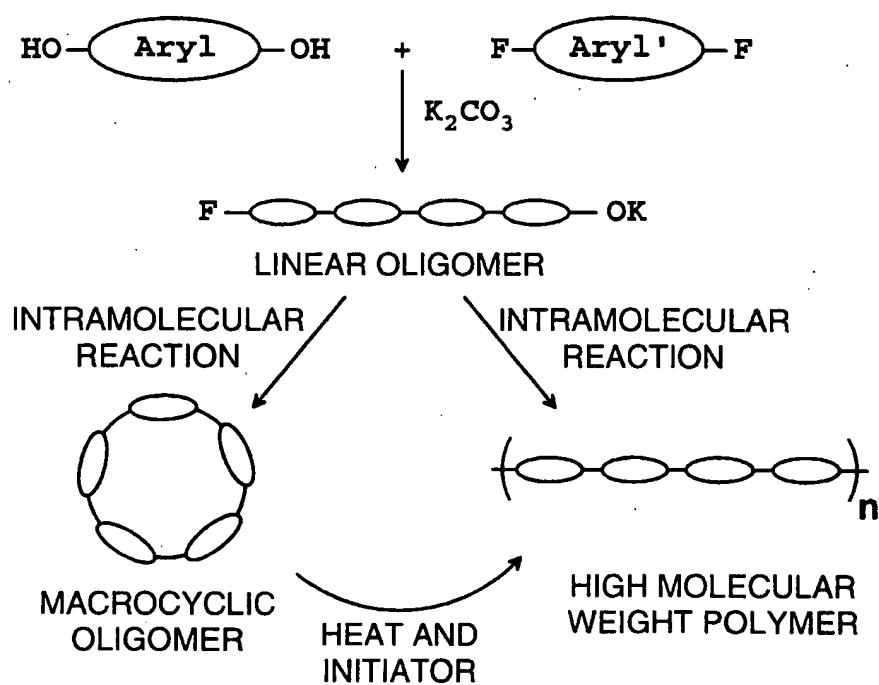
-35-

49. The nanocomposite of claim 48, wherein the nanocomposite comprises from between about 1% to about 10% (w/v) phenol formaldehyde polycyclic phosphonate, from between about 80% to about 99% (w/v) low melt viscosity polycarbonate and from between about 1% to about 10% (w/v) C<sub>12</sub>

5 ORMLAS.

50. The nanocomposite of claim 48, the nanocomposite comprising from between about 80% to about 99% (w/v) 6F-PAEPPC macrocycle and between from about 1% to about 10% (w/v) C<sub>12</sub> ORMLAS.

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SCHEMATIC OF THE FORMATION OF  
MACROCYCLE AND LINEAR POLYMER

FIG. 1

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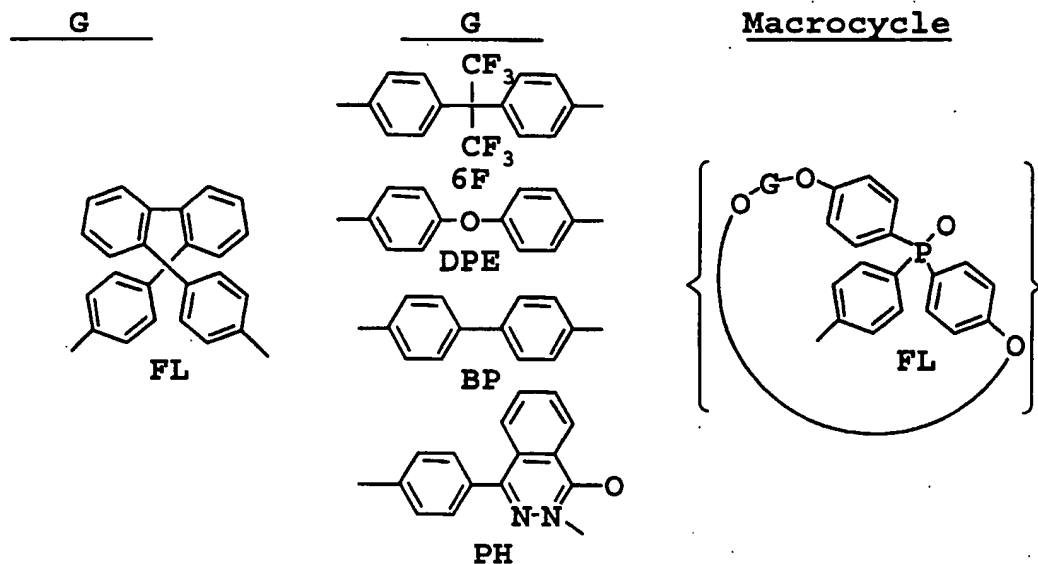


FIG. 2

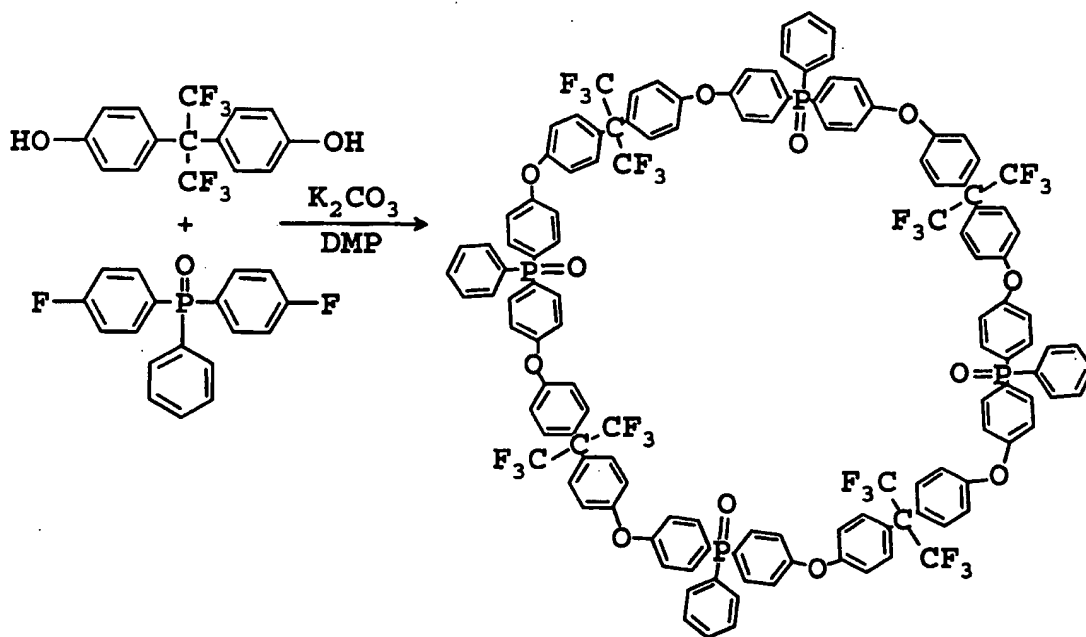


FIG. 3

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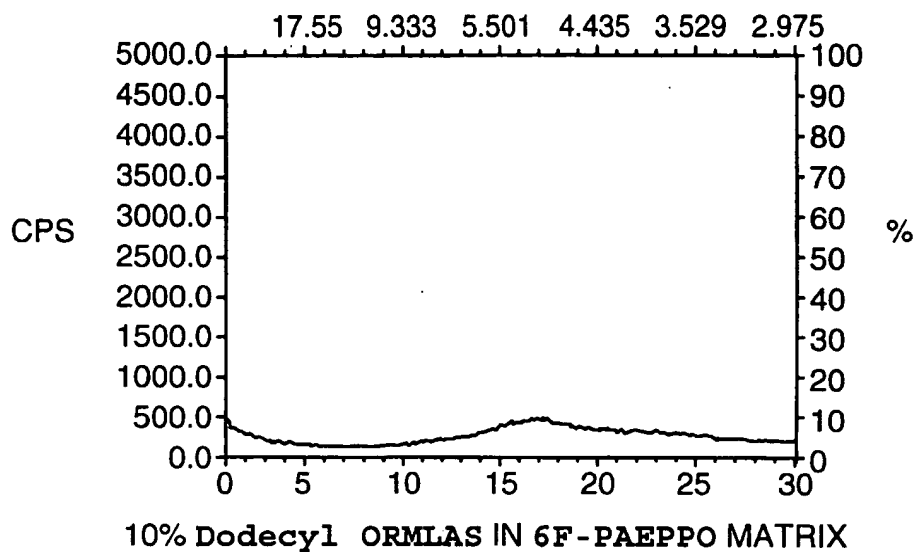


FIG. 4

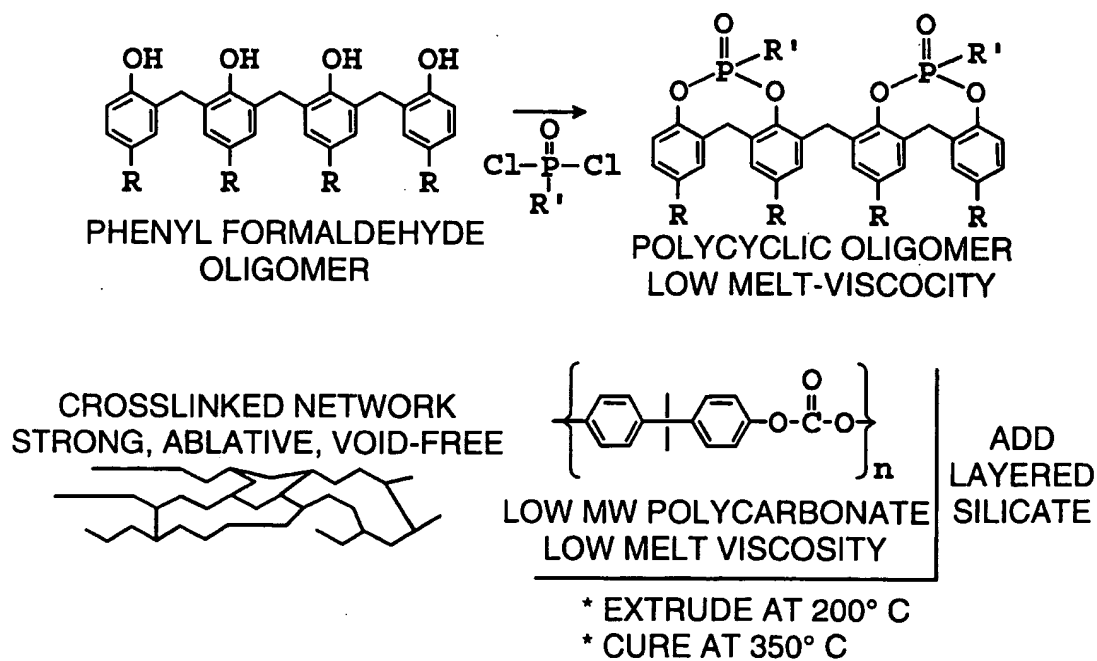


FIG. 5



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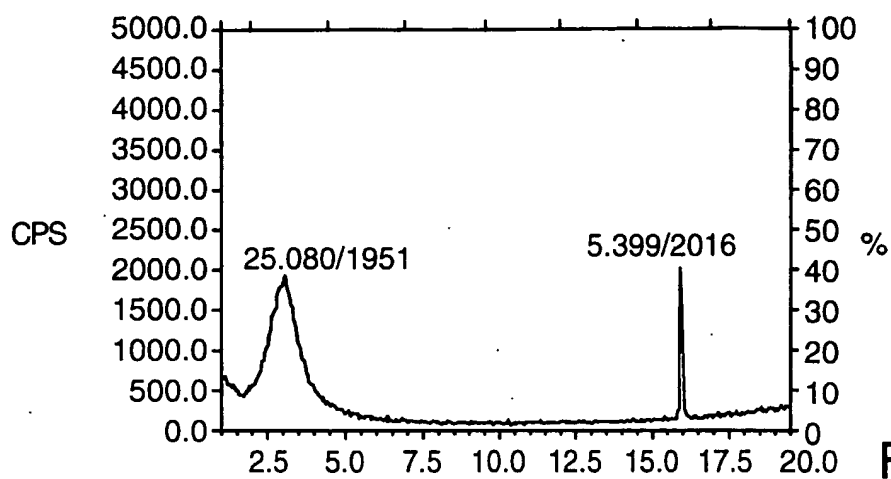


FIG. 6

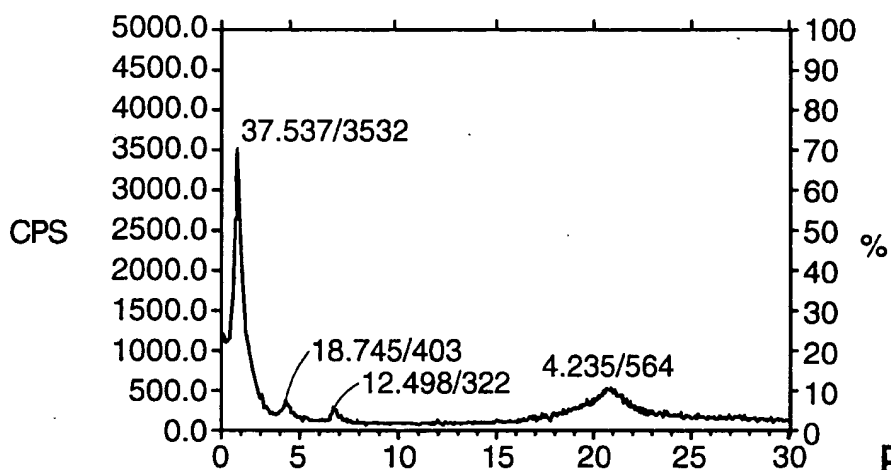


FIG. 7

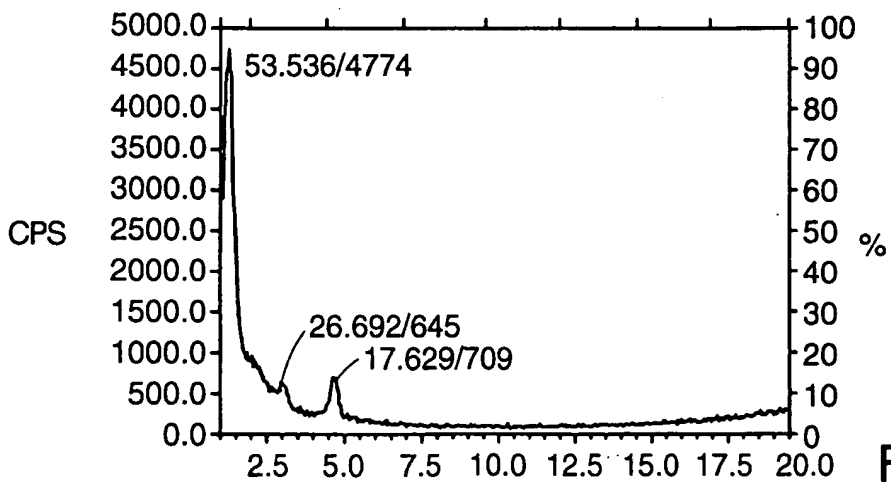


FIG. 8

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FIG. 9

# INTERNATIONAL SEARCH REPORT

International application No.

PCT/US99 /24957

## A. CLASSIFICATION OF SUBJECT MATTER<sup>6</sup>:

IPC 7 : C08K 3/34, 3/36

US CL : 524/442,444,445

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S : 524/442,444,445

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

NONE

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

WEST

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 5,514,734 A (MAXFIELD et al), 07 May 1996 (07.05.96), abstract and claims.	1-50
Y,P	US 5,849,830 A (TSIPURSKY et al), 15 December 1998 (15.12.98), abstract and claims.	1-50
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☐

Further documents are listed in the continuation of Box C.

☐

See patent family annex.

\* Special categories of cited documents:

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"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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"&" document member of the same patent family

Date of the actual completion of the international search  
10 January 2000 (10.01.00)

Date of mailing of the international search report  
04 February 2000 (04.02.00)

Name and mailing address of the ISA/

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